END

FILMED

DTIC

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

AD-A161 357

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
56		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
Spectroscopic and Electrochemical Studies of the Transition Metal Tetrasulfonated Phthalocyanines: Part V. Voltammetric Studies of Adsorbed Tetrasulfonated Phthalocyanines (MTsPc) in Aqueous Solutions	Technical Report
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
S. Zecevic, B. Simic-Glavaski, E. Yeager, A.B.P. Lever and P.C. Minor	N00014-83-K-0343

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Dept. of Chemistry Case Western Reserve University Cleveland, Ohio 44106 and York University, Downsview, Ontario, Canada	NR 359-451

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217	1 October 1985
	13. NUMBER OF PAGES
	11

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release; its distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Co-issued by the Case Western Reserve University and the York University groups.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Cyclic voltammetric measurements of adsorbed Fe- and Co-tetrasulfonated phthalocyanine (TsPc) and Co-phthalocyanine (Pc) have been carried out on ordinary pyrolytic graphite and silver electrodes at different solution pH ranging from 1 to 13. Many voltammetry peaks were found to be pH dependent with a slope of -59 mV/unit pH. In some instances this dependence was observed in alkaline or acid solutions only. Explanations for the various voltammetry peaks and their pH dependence are discussed. The influence of dioxygen and its reduction have also been examined.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE
1 JAN 73
S/N 0102-LF-014-6601

Unclassified

Spectroscopic and Electrochemical Studies of the Transition

Metal Tetrasulfonated Phthalocyanines:

Part V. Voltammetric Studies of Adsorbed Tetrasulfonated

Phthalocyanines (MTsPc) in Aqueous Solutions

by

S. Zecevic, B. Simic-Glavaski and E. Yeager

Case Western Reserve University
Case Center for Electrochemical Sciences
and the Department of Chemistry
Cleveland, Ohio 44106

and

A.B.P. Lever and P.C. Minor

York University
Department of Chemistry
Downsview, Ontario M3J 1P3 Canada

October 1, 1985

SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF TRANSITION METAL TETRASULFONATED PHTHALOCYANINES

PART V. VOLTAMMETRIC STUDIES OF ADSORBED TETRASULFONATED PHTHALOCYANINES (MTsPc) IN AQUEOUS SOLUTIONS

S. ZECEVIC *, B. SIMIC-GLAVASKI and E. YEAGER

Case Western Reserve University, Case Center for Electrochemical Sciences, and the Department of Chemistry Cleveland, OH 44106 (U.S.A.)

A.B.P. LEVER and P.C. MINOR

York University, Department of Chemistry, Downsview, Ontario, M3J 1P3 (Canada)

(Received 4th December 1984; in revised form 2nd July 1985)

ABSTRACT

Cyclic voltammetric measurements of adsorbed Fe- and Co-tetrasulfonated phthalocyanine (TsPc) and Co-phthalocyanine (Pc) have been carried out on ordinary pyrolytic graphite and silver electrodes at different solution pH ranging from 1 to 13. Many voltammetry peaks were found to be pH dependent with a slope of -59 mV/unit pH. In some instances this dependence was observed in alkaline or acid solutions only. The influence of oxygen has been also examined.

INTRODUCTION

Metallo-porphyrins and the related macrocycle metallo-phthalocyanines have been known for a long time both as homogeneous and heterogenerous catalysts in a wide range of chemical reactions [1–3]. Despite considerable effort, however, the catalytic mechanism is still not well understood. The macrocycles function as redox catalysts, metal complex changing oxidation state during the catalytic cycle. The catalytic activity of the complexes is dependent on the central metal ion involved and the total oxidation state of the complex. At least six different oxidation states have been observed through chemical and/or electrochemical reduction and oxidation of porphyrin or phthalocyanine systems [1,3].

Numerous studies have considered the redox electrochemistry of porphyrins and phthalocyanines [4–14], the majority with solution phase species. The redox poten-

---

* Permanent address: Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Yugoslavia.
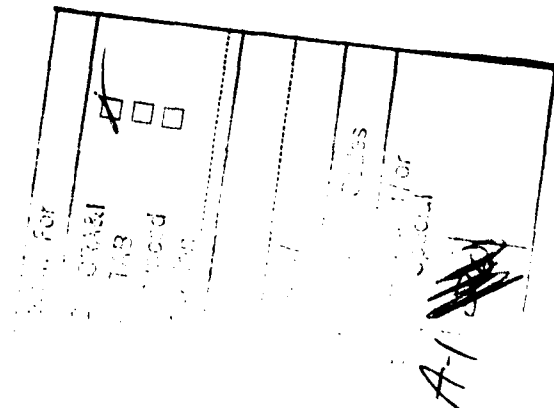
tials depend on factors such as the nature of the complex and its side chains, the central metal ion, the axial ligands, ion pairing, solvent and polymerization [10,13–15]. In most instances, in voltammetry studies, the redox peaks correspond to one-electron diffusion controlled processes. Because of the poor solubility of these compounds in water (unless some polar groups are introduced), organic solvents such as DMF, DMSO, and DMA have frequently been used.

Several electrochemical studies have been carried out with the complexes adsorbed or otherwise attached to an electrode surface [16–20]. Because of the interaction between the adsorbed molecule and the electrode surface, redox potentials differing from those in homogeneous solution may be expected. Furthermore, an electrode such as graphite with its functional groups acting as the axial ligand of the macrocycle can exert an additional influence on the redox potentials. Dioxygen interacting with the complex via axial coordination to the central metal ion or via peripheral bonding to the macrocycle ring can also influence the redox potentials (18–20).

The redox properties of Co- and Fe-tetrasulfonated phthalocyanine (–TsPc) adsorbed on graphite surfaces in aqueous solutions have been reported [16,17]. The potential range used in these previous investigations, however, was not sufficiently wide to indicate all the redox potentials of interest. The present work has been undertaken with the aim of further characterizing Co- and Fe-TsPc in aqueous solutions at various pH over a wider potential region including that suitable for O_2 reduction.

The iron and cobalt metallo-porphyrins and phthalocyanines have been found to be quite active catalysts for O_2 reduction [16–19,21]. The factors which make these two metals so effective are not clearly understood. Certain binary metal complexes such as the dicobalt face-to-face porphyrins which can form a dioxygen bridge have been shown to catalyze the overall 4-electron reduction of O_2 to H_2O in acid solutions [18]. A planar bicobalt dipyridyl complex which can form a dioxygen complex also catalyzes the 4-electron reduction of O_2 [22]. Fe-TsPc adsorbed on graphite has also been found to catalyze the overall 4-electron reduction in alkaline solution. Co-, Ni- and Cu-TsPc, however, catalyze the 2-electron reduction to peroxide in alkaline solutions and not the overall 4-electron reduction [16,21]. There are some relationships between macrocycle redox potentials and affinity towards reversible binding of oxygen in solution phases [23,24]. It is not yet established, however, whether such relationships exist when the complex is adsorbed on the electrode surface. Oxygen adduct formation with Co-TsPc in aqueous solutions, in alkaline pH [25,26] and also at pH 1 [27] has been reported. Although there is some controversy concerning the mechanism and products of the reversible oxygenation of aqueous Fe(II)-TsPc solutions [27–30], there is no doubt that Fe(II)-TsPc reacts with O_2. Recently, it has been proposed that Co-TsPc adsorbed in monolayers on platinum, gold and the basal plane of stress-annealed pyrolytic graphite may form a dioxygen bridged dimer TsPc–Co–O–O–Co–TsPc complex at potentials more positive than those for O_2 reduction [31] analogous to the oxygen adduct proposed to exist in aqueous solutions [25,26].

Although the aggregation of Fe-TsPc and Co-TsPc is well established, the nature of the dioxygen interaction with these complexes in solution as well as adsorbed on surfaces remains uncertain [25,34–40].

Cyclic voltammograms are reported in this paper for Fe- and Co-TsPc adsorbed on ordinary pyrolytic graphite and silver electrodes in helium and oxygen saturated aqueous solutions in the pH range 1–13. (The valencies indicated are those of the complex added to the solution from which the adsorption occurs.)

EXPERIMENTAL

The metallo-tetrasulfonated phthalocyanines Fe(III)- and Co(II)-TsPc were synthesized and purified according to the method of Weber and Busch [30]. The electrolytes were prepared from ultra pure grade sulfuric acid (Baker Ultrex), special low carbonate NaOH pellets (J.T. Baker) and analytical grade Na_2SO_4 (Fisher Scientific Co.) with triply distilled water.

An ordinary pyrolytic graphite (OPG) (Union Carbide) disk, 5 mm diameter, and a high purity silver disk (99.999%), 0.64 cm diameter, embedded in the end of Teflon rods were used as working electrodes. The electrode surfaces were polished with a water suspension of Al_2O_3 before every experiment. The last polishing was done with a particle size of 50 nm. The electrodes were then placed in an ultrasonic cleaning bath filled with triply distilled water for 5 min and finally rinsed with fresh water.

A gold foil (99.9% pure) and a saturated calomel electrode, placed in external compartments served as counter and reference electrodes, respectively. These compartments were separated from the bulk electrolyte with fritted glass disks. In addition a closed Teflon stopcock salt bridge (0.05 M Na_2SO_4) was used to connect the reference electrode compartment. The potential of the working electrode was controlled with a potentiostat (PARC-173) and wave form generator (PARC-175) and cyclic voltammograms were recorded using an X–Y recorder (Omnigraphic 2000).

All experiments were carried out at room temperature ($\sim 25°C$). Helium or nitrogen were purified using a series of traps consisting of silica gel, a de-ox catalyst (Alpha Ventron) and molecular sieves maintained at liquid N_2 temperature. Oxygen (Linde) was purified using a series of traps consisting of silica gel, Hopcalyte and molecular sieves.

The following procedure was employed in most experiments. The starting electrolyte was usually 0.05 M Na_2SO_4. After deaeration of this solution by bubbling N_2 or He for at least 30 min, 1 ml of the appropriate TsPc stock solution (10^{-3} M in water) was added to 100 ml of the electrolyte and a 10^{-5} M solution thereby obtained. Cyclic voltammograms were then recorded and a few milliliters of the electrolyte were withdrawn from the cell to measure pH. In order to change the pH of the electrolyte, 1 ml of concentrated H_2SO_4 or NaOH was added as appropriate. The voltammetry was then repeated, the pH measured again and so on. In this way cyclic voltammetry was performed in the pH range 11.3 to 12.8. In the pH range

from 6 to 9 the measurements were completed under buffered conditions using appropriate borate and phosphate solutions.

In addition to water soluble Co- and Fe-TsPc, Co(II)-Pc was also examined. In this case preadsorption was performed by putting a drop of 10^{-5} M Co(II)-Pc pyridine solution onto the electrode surface. After ca. 5 min the electrode surface was rinsed with neat pyridine, then with ethanol and finally with distilled water. Under such circumstances the initial species on the electrode is PcCo(II)Py [41].

All of the voltammograms were recorded after sufficient cycling to achieve steady state conditions.

RESULTS

Experiments under an inert atmosphere

Immediately after addition of M-TsPc to the supporting electrolyte, the first potential sweep over the given range (e.g., -0.8 to 0.3 V vs. SCE in 10^{-5} M Fe(III)-TsPc pH 10.7) at 200 mV/s gave hardly detectable voltammetric peaks. The height of the peaks increased with time and the steady-state was attained after about 30 min. Rather similar observations were reported by Nikolic et al. [31] while investigating the electrochemical behavior of 10^{-5} M aqueous solutions of Co(II)- and Fe(III)-TsPc using Pt and Au electrodes. They found that during potential cycling (in the range of 0.0–0.8 V vs. α-Pd/H electrode) at a sweep rate of 100 mV/s, voltammetric peaks of the hydrogen adsorption/desorption and oxide formation/reduction processes decreased with time with adsorption of the macrocycles. The adsorption equilibrium was established after 30 min. This suggests that adsorption of the macrocycle can displace other sorbents. Slow adsorption has also been reported by Brown et al. [42] investigating the electrochemical behavior of 10^{-6} M, 9,10-phenanthrenequinone and 10^{-4} M Ru(NH$_3$)$_6^{3+}$ ion on a pyrolytic graphite electrode in 1 M CF$_3$COOH. They found that complete adsorption of the former takes more than 50 min, whereas the wave corresponding to a redox process of the Ru(NH$_3$)$_6^{3+}$ ion, which does not adsorb on the graphite surface, does not change with time. To obtain well defined voltammetry peaks with M-TsPc, potential cycling was necessary, the best results being obtained with high sweep rates, e.g., 20 V/s. An OPG electrode standing at open-circuit potential in a Fe(III)-TsPc at potentials between peaks 3 and 4 in Fig. 1 did not exhibit any significant voltammetry peak even after 2 h, no matter what the Fe(III)-TsPc concentration or pH or atmosphere (O$_2$ or He). In contrast to OPG, fairly good peaks could be obtained on silver electrodes which stood in Fe(III)-TsPc solution on open circuit for a few min, but potential cycling still significantly increased the peak heights in the voltammogram. Evidently the slow achievement of steady-state is not due to the low diffusion coefficient of Fe(III)-TsPc, but to kinetic factors, and the preparation, via cycling, of a clean surface.

Typical cyclic voltammograms of an OPG electrode in N$_2$ saturated 10^{-5} M Fe(III)-TsPc alkaline solution are shown in Fig. 1. For clarity, redox couples
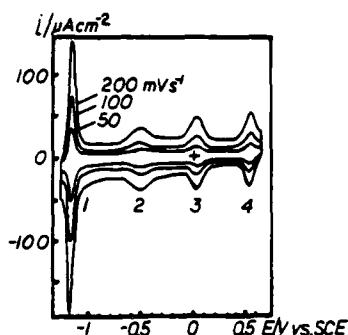
Fig. 1. Cyclic voltammograms on OPG in 0.05 M Na$_2$SO$_4$, pH 10.7 (N$_2$-saturated) containing 10^{-5} M Fe(III)-TsPc at different scan rates in mV/s.

observed in alkaline solution are labelled 1, 2, 3..., and those observed in acid solution A, B, C..., with 1 and A the most negative couple observed. It does not necessarily follow that couples 1 and A, etc, arise from the same redox process. The anodic as well as the cathodic peak currents are directly proportional to the sweep rate over the range examined (20–500 mV/s). The peak potential separation ($E_{p,anodic} - E_{p,cathodic}$) is very small (less than 10 mV) for all peaks. A slightly higher value is observed for peak 1 at high sweep rates. Otherwise, the peak separation is practically independent of the scan rate. There is no stirring dependence of the peaks heights and no contribution of unadsorbed Fe(III)-TsPc in the solution phase. All these observations indicate that the voltammetric peaks are due to Faradaic processes involving adsorbed species. Identical results were obtained after the Fe(III)-TsPc solution was replaced with the supporting electrolyte. The adsorbed Fe-TsPc, however, diffuses from the electrode surface with time and the magnitude of the peak currents decreases. A progressive decrease of peak heights is also observed when the upper limit was more positive than the potential of peak 4, or more negative than the potential of peak 1. 1 or 2 min poised at one of these potential limits causes complete disappearance of the peaks, possibly due to decomposition of the ligand, demetallization or desorption.

The charge involved in the redox processes of the adsorbed Fe-TsPc can be estimated from the area under the peaks. Charges of 57, 13, 16 and 17 μC/cm^2 have been determined corresponding to peaks 1, 2, 3 and 4, respectively. The last three values are in reasonably good agreement with the 13 μC/cm^2 reported by Zagal on OPG [21]. Of particular interest is the number of electrons (n) involved in each of the redox processes corresponding to these peaks. Since these peaks are reversible, Nernst behavior is expected. Thus, for a given peak with a redox reaction of the form

$$Ox + n\,e^- \rightarrow R \tag{1}$$

the reversible potential assuming ideallity, is

$$E = E_0 - (RT/nF) \ln[\theta_R/\theta_{Ox}] \tag{2}$$

where θ_R is the fraction of the adsorbed species in the reduced form, θ_{Ox} is the fraction in the oxidized form and E_0 is the standard electrode potential corresponding no $\theta = 1/2$. The voltammetric peaks are sufficiently separated that each peak can be treated separately with eqn. (2) and $\theta_R + \theta_{Ox}$ can be taken as equal to unity. For such a system, the peak current in the voltammetric curves is related to the sweep rate by the equation [16,43]

$$i_p = (n^2F^2/4RT)v\Gamma \tag{3}$$

where Γ is the total surface concentration of the adsorbed species in mol/cm^2 and v is the potential scan rate. The charge Q under a given voltammetric peak (either cathodic or anodic) is related to Γ through the equation

$$Q = nF\Gamma \tag{4}$$

Thus the value for n is given by

$$n = i_p 4RT/QFv \tag{5}$$

Using the experimental values for i_p/Q, eqn. (5) yields values of 0.8 for each of the four peaks, indicating that one electron per molecule is involved in each of the surface redox processes. The deviation from a value of 1 is probably caused by the non-ideality of the system (e.g., slow kinetics). Possible evaluations for the higher charge under peak 1 even though $n = 1$ will be discussed later.

The voltammograms shown in Fig. 1 retain approximately this shape in the alkaline region (pH 8–13). In acid solutions, however, peak D becomes smaller in magnitude as the pH decreases and, at pH less than 4, disappears. In addition, scanning to an upper limit more positive than the potential at which peak D is expected to appear gives rise to irreversible oxidation modifying the remaining three peaks (see Fig. 2). Hence, to observe the first three peaks, the upper limit must not be much more positive than the potential of peak C. In these solutions peak C becomes broader, less symmetrical and at pH 1 the complementary cathodic peak is too broad to determine its position precisely.

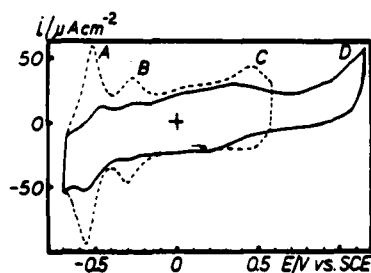Figure 3 presents typical cyclic voltammograms on OPG in N_2 saturated 10^{-5} M

Fig. 2. Cyclic voltammograms on OPG in 0.05 M Na_2SO_4, pH 3.5 (N_2-saturated) containing 10^{-5} M Fe(III)-TsPc at diffferent upper limits; scan rate 200 mV/s.
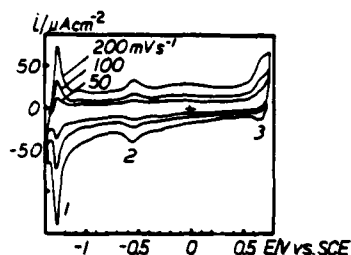
Fig. 3. Cyclic voltammograms on OPG in 0.05 M Na_2SO_4, pH 10.7 (N_2-saturated) containing 10^{-5} M Co(II)-TsPc at different scan rates in mV/s.

Co(II)-TsPc alkaline solution. The linear propostionality of peak current to scan rate, small peak potential separation and negligible influence of unadsorbed Co-TsPc from the solution phase have also been observed in this case, indicating redox processes involving adsorbed species. Only three well defined peaks, however, are observed in this case. The cathodic limit significantly influences the shape of the voltammograms. When less negative than the potential of peak 1, the very broad wave between peaks 2 and 3 disappears and these become as sharp as those in the case of Fe-TsPc (see Fig. 4). From the scan rate dependence of the peak currents densities and the corresponding transferred charge, one-electron transfer appears to be involved in each case.

In contrast to Fe-TsPc, in acid solution Co(II)-TsPc gives the same number of peaks as in alkaline solution. Peak B, however, becomes very broad which is not the case for Fe-TsPc (see Fig. 5).

Co-Pc preadsorbed in OPG from pyridine solution shows very similar behavior to that of Co-TsPc. The number of peaks is the same in acid solutions (see Fig. 6), but peak 1 is missing in alkaline solutions most likely because it is out of the voltage range. All peak positions are apparently equally shifted by about 80 mV towards more negative potentials relative to the unsubstituted species.

The voltammetry curves for adsorbed H_2-TsPc have also been examined and contain interesting information which will be discussed in a future paper.
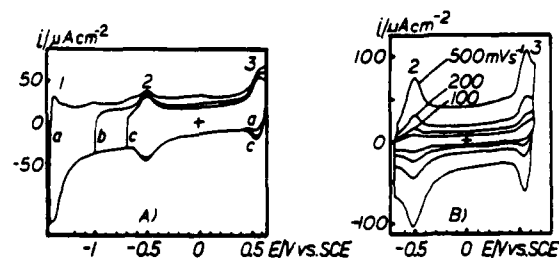

Fig. 4. Cyclic voltammograms on OPG in 0.05 M Na_2SO_4, pH 12.8 (N_2-saturated) containing 10^{-5} M Co(II)-TsPc at different lower limits (scan rate 200 mV/s) (A); and different scan rates in mV/s (B).
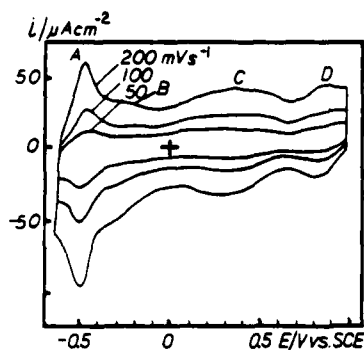
8

Fig. 5. Cyclic voltammograms on OPG in 0.05 M Na$_2$SO$_4$, pH 1.3 (N$_2$-saturated) containing 10^{-5} M Co(II)-TsPc at different scan rates in mV/s.

A similar feature of the adsorbed Fe- and Co-TsPc complexes is the pH dependence of the voltammetry peaks (Fig. 7). In most instances, the slope of the plots of peak potential vs. pH is ca. -59 mV/unit pH. A similar value (-57 mV/pH) has been reported by Zagal [21] for peak 3 of adsorbed Fe-TsPc and also by Brown et al. [42] for Fe-proto-porphyrin IX on graphite (-60 mV/pH).

Experiments with a silver electrode in acid solutions gave similar voltammograms to those on OPG (see Fig. 8). However, because of silver dissolution at positive potentials only the two most negative peaks could be observed. The peak currents on Ag are directly proportional to the scan rate within the range examined (20–500 mV/s). The peak potential separation between the positive and negative sweeps is higher (e.g., 40 mV at 100 mV/s) than on OPG and increases slightly with scan rate. In contrast to the OPG surface, the preadsorbed layers of the macrocycle are more stable. On Ag, the peak currents did not change significantly for several hours after the TsPc solution had been replaced by a solution containing only the supporting electrolyte. With the OPG electrode the peak currents of preadsorbed Fe-TsPc in
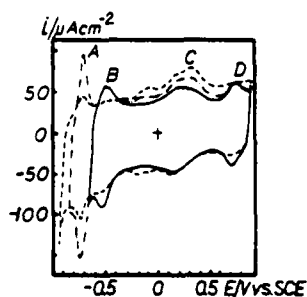

Fig. 6. Cyclic voltammograms of Co-Pc pre-adsorbed on an OPG electrode in 0.05 M Na$_2$SO$_4$, pH 3.3 (N$_2$-saturated) at different lower limits; scan rate 500 mV/s.
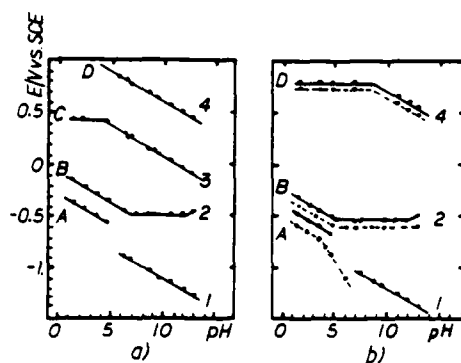
Fig. 7. Average cathodic/anodic voltammetric peak potentials as a function of pH of electrolyte containing 10^{-5} M Fe-TsPc or Co-TsPc. (a) Fe-TsPc; (b) Co-TsPc, Co-Pc (●●●).

acid solutions at pH < 4 are significantly smaller than in the presence of Fe(III)-TsPc in solution. On Ag, all of the peaks shift towards negative potentials with increasing pH with a slope of −60 mV/pH. At the same time they become broader, their magnitudes decrease and at pH > 7 the peaks do not appear. However, desorption of the complexes does not occur in alkaline solutions since a reacidification of the supporting electrolyte regenerates the peaks. Moreover, good surface enhanced Raman spectra have been obtained in alkaline solutions indicating the presence of the adsorbed macrocycles [27].

While voltammetric curves are readily obtained with Fe and Co-TsPc dissolved ibn an organic solvent such as acetonitrile. Efforts to obtain the voltammetric curves for the aqueous solution phase Fe- and Co-TsPc species have been unsuccessful even using quite concentrated solutions of these species (10^{-2} M). The difficulty in obtaining voltammetric curves may be caused by substantial aggregation in the concentrated aqueous solution and low diffusion coefficients in the dilute solutions.
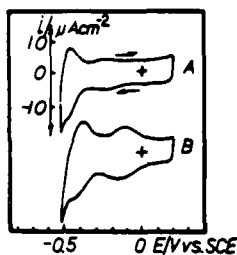

Fig. 8. Cyclic voltammograms of preadsorbed TsPc on a silver electrode in 0.05 M H$_2$SO$_4$ (He-saturated) (A) Co-TsPc (B) Fe-TsPc Scan rate 100 mV/s; electrode area 0.32 cm^2.
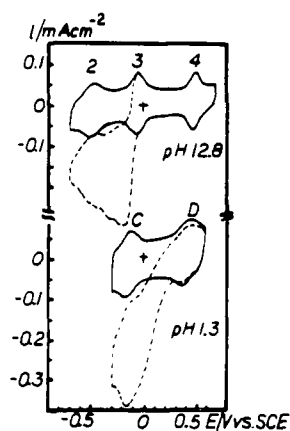
Fig. 9. Cyclic voltammograms on OPG in 0.05 M Na$_2$SO$_4$, pH 12.8 and pH 1.3 containing 10^{-5} M Fe(III)-TsPc under N$_2$ atmosphere (————) and in the presence of O$_2$ (●●●); scan rate 500 mV/s; no rotation.

Experiment withs O$_2$ present

The effect of O$_2$ on cyclic voltammograms at the OPG electrode in alkaline solutions containing 10^{-5} M Fe(III)-TsPc is shown in Fig. 9. The O$_2$ reduction begins more negative than the reduction process corresponding to peak 3, but there is no change in the voltammogram at potentials more positive than that of peak 3. In
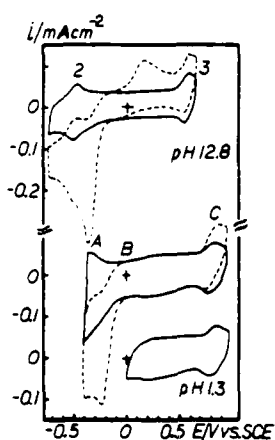

Fig. 10. Cyclic voltammograms on OPG in 0.05 M Na$_2$SO$_4$, pH 12.8 and pH 1.3 containing 10^{-5} M Co(II)-TsPc under N$_2$ (————) and O$_2$ (●●●); scan rate 500 mV/s; no rotation. (Note: at pH 1.3 when the lower limit is 0.0 V, there is no difference between N$_2$ and O$_2$ voltammograms.)
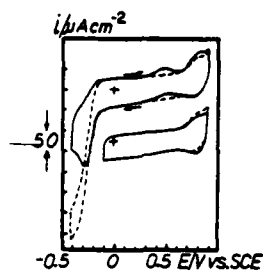
Fig. 11. Cyclic voltammograms on OPG in borate buffered solution, pH 8.7 containing 10^{-5} M Co(II)-TsPc in the presence of O_2 (————) No rotation; (●●●) rotation rate 1600 rpm.

less alkaline solution, as well as in acid, O_2 reduction starts at slightly more negative potentials than that of the reduction process of peak C.

In contrast to Fe-TsPc, the voltammetric curve for Co-TsPc is significantly affected by the presence of O_2. In alkaline solutions (see Fig. 10, in addition to changes in the voltammetric curve in the region of peak 3, an irreversible anodic peak appears. In acid solution (pH 1) this wave is not observed, but changes in the region of peak 3 are still present. If the lower limit is positive enough to avoid oxygen reduction, the influence of O_2 is not observed. These observations have been made without rotation of the OPG electrode. If the electrode rotates (e.g., 1600 rpm), these effects disappears (see Fig. 11). We conclude that the extra anodic peak is derived from the oxygen reduction product H_2O_2. Separate experiments performed under N_2 or He atmosphere in the presence of 10^{-4} M H_2O_2, in the region where O_2 reduction does not take place, confirm this explanation (see Fig. 12).
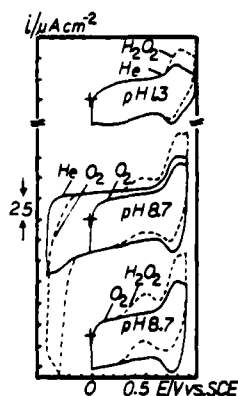

Fig. 12. Cyclic voltammograms on OPG in borate buffered solution, pH 8.7 and 0.05 M Na_2SO_4, pH 1.3 (both containing 10^{-5} M Co(II)-TsPc) under He atmosphere in the presence of O_2; and under He atmosphere in the presence of 10^{-4} M H_2O_2; scan rate 500 mV/s; no rotation.

DISCUSSION

Aggregation

The UV–visible absorption spectra [44] of the Fe(III)-TsPc in solution at concentrations of $\sim 10^{-5}$ M provide evidence that most of the complex is associated in acid (0.05 M H_2SO_4) and alkaline (0.1 M NaOH) solutions, using as a criterion the predominance of the peak at ~ 630 nm over that at ~ 670 nm. For the 10^{-5} M Co(II)-TsPc the 620 nm peak is predominant ovei the ~ 665 nm peak in 0.05 M H_2SO_4 but not in).1 M NaOH, indicating that the association is much less in the alkaline solution than in the acid solution, probably because of charge repulsion between the SO_3^- and OH^- groups. The difference in the behavior of the FeTsPc and CoTsPc systems may arise from the formation of a strongly bound μ-oxo complex in the former case, constraining thereby the close association of two phthalocyanine units in alkaline solutions. CoTsPc does not form a μ-oxo species. A monomer–dimer equilibrium may be involved with Co(II)-TsPc in neutral aqueous solutions of $\leq 10^{-5}$ M with an equilibrium constant of $K = 2.05 \pm 0.05 \times 10^{-5}$ M^{-1} as determined by Schelly et al. [36] using the 665 nm peak as a measure of the monomer concentration. At higher concentrations, as well as higher ionic strengths ($> 10^{-4}$ M), higher association or polymerization than the dimer is apparently involved [34–40].

Some visible reflectance spectral data have been reported for Fe- and Co-TsPc adsorbed on the basal plane of highly ordered graphite and platinum [31]. The data are of sufficient quality to use as a criterion for association only in the instance of the preadsorbed Fe-TsPc in 0.1 M NaOH. The spectra with both the graphite and platinum resemble the solution phase spectrum with the 630nm peak shifted to ~ 635 nm and predominant over the longer wavelength peak at ~ 665 nm. This provides evidence for. association of the adsorbed Fe-TsPc even from alkaline solutions, as has been observed for the solution phase.

The pK values for the ionization of the sulfonic acid groups on the TsPc ligand are not known. The pK of benzene sulfonic acid is 0.7 [45] and the values for the sulfonic acid groups in the TsPc ligand are also probably very low. While the pK should increase as the successive sulfonic groups become ionized, this shift of the pK values is probably quite small since the groups are widely separated and the charge can be compensated by cations of the supporting electrolyte (Na$^+$). Thus, except in very acid solutions, the four sulfonic acid groups are expected to be ionized. The large negative charge should suppress the tendency for aggregation but this charge is probably, in part, offset by association with Na$^+$ ions of the 0.05 M Na$_2$SO$_4$ supporting electrolyte.

The Raman spectra have also been obtained for Co- and Fe-TsPc adsorbed on silver, taking advantage of the large surface enhanced Raman scattering on this surface, as well as resonant or pre-resonant Raman enhancement [46–48]. These Raman spectra resemble those of the corresponding aqueous solution phase species at $\sim 10^{-5}$ M [49]. Raman polarization data obtained on the low index surfaces of

single crystal silver (without activation) [50] confirmed the earlier hypothesis [48] that the TsPc ligand is perpendicular to the silver surface. The similarity of the voltammetry curves for Co- and Fe-TsPc adsorbed on graphite and silver suggest that the orientation of the TsPc ligand may be the same on both of these surfaces. Such an orientation permits the dissociation of the aggregates without simultaneous desorption and loss of part of the adsorbed layer into the bulk solution. Unfortunately, the Raman spectra obtained with visible frequency laser lines are not very sensitive to axial ligands.

The voltammetry peaks are much better defined for the adsorbed TsPc complexes on OPG in alkaline than in acid solutions, and quite reversible. This suggests a difference in the structure of the adsorbed layers in alkaline and acid electrolytes. One possibility is that the adsorbed Co- and Fe-TsPc are monomeric in alkaline solutions, while dimers are involved in acid solution. The spectroreflectance data, however, provides evidence that at least for the adsorbed Fe-TsPc, a dimeric species is involved in alkaline solution. A more likely possibility is that the predominant adsorbed Co-TsPc, as well as Fe-TsPc, species are the dimers in alkaline solution and that the adsorbed layers involve even higher aggregates in acid media.

Two limiting electrochemical situations can be envisaged for the adsorbed layers involving aggregations. Assume dimeric aggregation for simplicity. One electron reduction (or oxidation) of the dimer occurs and there is a rapid dis-aggregation followed by reduction (or oxidation) of the other molecule. If the disaggregation is fast on the electrochemical time scale, the voltammogram would appear like that of an unaggregated species. If the dis-aggregation is slow on the electrochemical time scale (or does not occur), then a second wave should be seen, corresponding to the reduction (oxidation) of MPc in a partially reduced (oxidized) mixed valence dimer. This has recently been discussed briefly by Kadish in his consideration of $(CN)_8PcZn$ [51]. Thus for this situation a pair of peaks is expected. More subtle aspects of the electrochemistry of aggregated phthalocyanines will be discussed elsewhere [52].

Peak assignment in alkaline media

We shall first discuss the voltammetric curves in alkaline solutions, where the behavior is very well defined, with 3 or 4 reversible redox couples.

Fe-TsPc. Previous experience with FePc systems [8,10,13] shows that the FePc systems can exist in Fe(I), Fe(II) and Fe(III) redox states. The Pc ring in its normal oxidation state carries two negative charges (written Pc(−2)) using the nomenclature outlined in ref. 53 and not including the charge associated with the ionized sulfonic acid groups. In the potential scan region discussed here, the ring may be oxidized (cation radical Pc(−1)), or reduced (anion radical Pc(−3)). On the basis of solution electrochemical studies [9,10,15,54], the peaks observed in Figs. 1–3 can be assigned as follows (omitting axial ligands):

Peak 4: Fe(III)TsPc(−1)/Fe(III)TsPc(−2)
Peak 3: Fe(III)TsPc(−2)/Fe(II)TsPc(−2)
Peak 2: Fe(II)TsPc(−2)/Fe(I)TsPc(−2)
Peak 1: Fe(I)TsPc(−2)/Fe(I)TsPc(−3)

The unusually high charge under peak 1 is considered later.

Under an oxygen atmosphere, reduction is expected to occur at, or slightly negative of, the Fe(III)TsPc(−2)/Fe(II)TsPc(−2) couple, since air oxidation of Fe(II)Pc species has been observed [10,33]. This reduction is seen to occur at peak 3, corresponding to the reduction of Fe(III)TsPc in alkaline solution (Fig. 9a). Uv/vis spectroelectrochemical studies as a function of pH have also been carried out in a thin layer cell with a solution of FeTsPc (and CoTsPc) using a gold minigrid. These results, which will be discussed elsewhere [55], are in agreement with the peak assignments shown above.

Co-TsPc. Co-TsPc systems can also exist in the Co(I), Co(II) and Co(III) redox states [9,11,13,41,52,56,57]. The Co(III)TsPc(−2)/Co(II)TsPc(−2) couple is very sensitive to the presence or absence of axial ligands because Co(III)TsPc(−2) is very unstable in the absence of strong donor (solvent or supporting electrolyte anion) molecules [41,52]. Water is a relatively weak ligand towards both Co(II) and Co(III) and the Co(III)TsPc(−2)/Co(II)TsPc(−2) couple is certainly found above 0.0 V vs. SCE. Thus peak 2 is reasonably associated with Co(II)TsPc(−2)/Co(I)TsPc(−2) since it is too negative for the Co(III)/Co(II) couple. Peak 1 by analogy with the Fe-TsPc system is assigned as reduction to the anion radical.

Peak 3 presents certain problems in assignment. In the absence of strongly coordinating ions, the oxidation couple Co(II)TsPc(−1)/Co(II)TsPc(−2) may lie below (more negative than) the Co(III)TsPc(−2)/Co(II)TsPc(−2) couple [52,58]. Thus peak 3 may correspond to either of these two possibilities. In alkaline medium the OH⁻ ion should act as a good counter anion (and axial ligand) for Co(III). It is reasonable to associate peak 3 with the Co(III)TsPc(−2)/Co(II)TsPc(−2) couple in alkaline medium especially as it shows a −95 mV/unit pH slope. Oxygen reduction in alkaline medium, however, occurs significantly negative of this peak. Note that the pH dependence of these couples parallels exactly that for FeTsPc supporting parallel assignments.

Thus the following scheme supported by solution spectroelectrochemistry [55] is proposed for pH > 7:

Peak 3: Co(III)TsPc(−2)/Co(II)TsPc(−2)
Peak 2: Co(II)TsPc(−2)/Co(I)TsPc(−2)
Peak 1: Co(I)TsPc(−2)/Co(I)TsPc(−3)

Peak assignment in acid media

The voltammogram recorded in acid media can be quite voltage window dependent, as shown in Fig. 2, and the peaks may be broad all ill-defined. It seems reasonable, however, to associate peaks C and D in acid media for FeTsPc with peaks 3 and 4 in alkaline media.

Since it is unlikely that OH⁻ will bind to Fe(II)Pc, it is not surprising that the slope of the Fe(II)Pc/Fe(I)Pc couple in alkaline medium (peak 2) is zero. It is strange however that the slope in the acid medium is −59 mV/unit pH (peak B). It

is possible that peak B corresponds with the couple Fe(II)TsPc(−2)/[Fe(II)Ts-Pc(−3)]⁻, i.e. reduction of the Pc ligand while maintaining the iron in oxidation state 2. However our spectroelectrochemical and esr studies in solution negative of peak B [55] do not support this hypothesis, but rather point towards the Fe(II)TsPc(−2)/[Fe(I)TsPc(−2)]⁻ couple as in alkaline solution. However the possibility of reduction of Fe(II)TsPc(−2) occurring to a species more completely represented as a hybrid of reduced metal and reduced ligand should be recognized.

It is difficult to study the solution spectroelectrochemistry of FeTsPc, negative of peak A because of solute decomposition. Similarly attempts to widen the potential window beyond −0.7 V in acid media, in the adsorbed state, were unsuccessful due to drastic irreversible changes. However, we were able to study this region of the voltammagram in solution spectroelectrochemical studies of CoTsPc [55]. These studies clearly show that peak A involves a reduction step to Co(I)TsPc(−3) subsequent to the reduction process at peak B. Thus assuming the solution and adsorbed behavior are comparable, peaks A and B involve the couples:

B   Co(II)TsPc(−2)/Co(I)TsPc(−2)
A   Co(I)TsPc(−2)/Co(I)TsPc(−3)
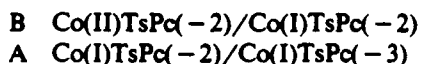
Given the close similarity in behavior between Co and FeTsPc (see Fig. 7) it is reasonable to assume an analogous assignment for peaks A and B in the latter species. Similarly, peaks C and D may be assigned as follows, also with support from spectroelectrochemistry (55):
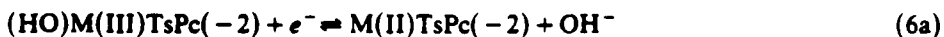
D   Co(III)TsPc(−2)/Co(II)TsPc(−2)
D   Fe(III)TsPc(−1)/Fe(III)TsPc(−2)
C   Fe(III)TsPc(−2)/Fe(II)TsPc(−2)
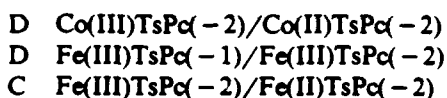
Previous solution studies have shown that the potential of the Co(III)/Co(II) couple is extremely sensitive to the nature of the axial ligand, and to variation in coordination number from five to six [14,15,41,52]. The C region in Co-TsPc (Fig. 6) probably reflects the existence of variously axially coordinated CoTsPc species.
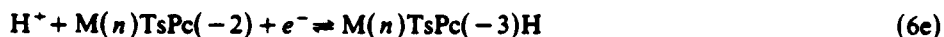
According to the development above, peaks 1 and A belong to the same redox process yet there is a discontinuity as a function of pH (Fig. 7). We defer discussion until the following section.

pH dependence

In Fig. 7 is displayed the pH dependence of these various peaks. Most show an approximate −59 mV/unit pH slope indicative of one proton or one hydroxyl group being involved in the redox couple equilibrium.

The following general equilibria would be expected to show such a dependence:

$$(HO)M(III)TsPc(-2) + e^- \rightleftharpoons M(II)TsPc(-2) + OH^- \tag{6a}$$

16

$$(HO)M(II)TsPc(-1) + e^- \rightleftharpoons M(II)TsPc(-2) + OH^- \tag{6b}$$

$$H^+ + M(n)TsPcH_m(-2) + e^- \rightleftharpoons M(n)TsPcH_{m+1}(-3) \tag{6c}$$

$$H^+ + M(n)TsPcH_m(-3) + e^- \rightleftharpoons M(n)TsPcH_{m+1}(-4) \tag{6d}$$

$$H^+ + M(n)TsPc(-2) + e^- \rightleftharpoons M(n)TsPc(-3)H \tag{6e}$$
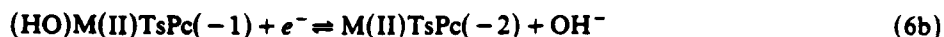
The number of sulfonic acid protons is assumed constant, and is omitted, except in examples (6c) and (6d). Redox reaction (6a) reflects the binding of a hydroxyl group to M(III) in basic medium. Reaction (6b) reflects the likelihood that for the positively charged cation radical, a hydroxyl group will bind to the metal to equalize the charge, even where the metal is divalent. Reactions (6c) and (6d) reflect the acid-base behavior of the pendant sulfonic acid residues in TsPc. Reaction (6e) is a general example of protonation at bridgehead aza nitrogen atoms. They are weakly basic ($pK_a \sim 2$) [1]. These would not be expected to contribute to the pH dependence except perhaps for the negatively charged TsPc resulting from the one electron reduction.

Essentially all of the redox processes discussed earlier display a -59 mv/unit pH slope dependence because of one of the above type redox reactions. In alkaline solution it is appropriate to replace H^+ by H_2O on the left hand side of these equations and to add an OH^- to the right hand side.
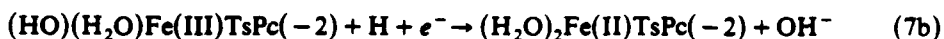
There are several regions in Fig. 7, however, where the pH dependence ceases. Thus the Fe(III)TsPc/Fe(II)TsPc couple (Peak C) shows no pH dependence in strong acid media (below pH 4). In this case there is no binding of OH^- to Fe(III). All four sulfonic acid groups are probably still completely ionized down to pH values approaching 1.

As an example, the following more detailed equations may be used to describe the pH dependence seen in Fig. 7 for Fe-TsPc. The equations (7a–7g) are representative, since the actual species may be aggregated in some cases.
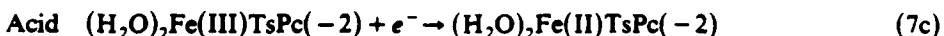
Peak 4: pH > 4

$$(HO)_2Fe(III)TsPc(-1) + H^+ + e^- \rightarrow (HO)(H_2O)Fe(III)TsPc(-2) \tag{7a}$$

Peak C: pH > 4

$$(HO)(H_2O)Fe(III)TsPc(-2) + H + e^- \rightarrow (H_2O)_2Fe(II)TsPc(-2) + OH^- \tag{7b}$$

Peak 3: pH < 4

$$Acid \quad (H_2O)_2Fe(III)TsPc(-2) + e^- \rightarrow (H_2O)_2Fe(II)TsPc(-2) \tag{7c}$$

Peak B: pH < 6

$$Acid \quad (H_2O)_2Fe(II)TsPc(-2) + H^+ + e^- \rightarrow \left[(H_2O)_2Fe(I)TsPc(-2)\right]^- H^+ \tag{7d}$$

Peak 2: pH > 6

$$(H_2O)_2Fe(II)TsPc(-2) + e^- \rightarrow (H_2O)_2Fe(I)TsPc(-2) \tag{7e}$$

Peak 1: pH > 5

$$(H_2O)_2Fe(I)TsPc(-2) + H_2O + e^- \rightarrow \left[(H_2O)_2Fe(I)TsPc(-3)\right] + OH^- \tag{7f}$$
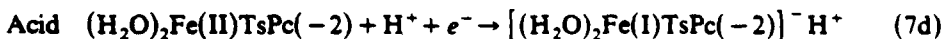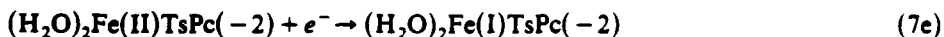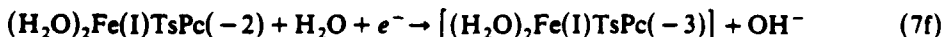
These reactions are based on the assumption that the metal ion may become six-coordinate, and, therefore, that the phthalocyanine unit is bound edgeway on the electrode as discussed earlier. Note, however, that a similar set of equilibria could be written if one coordination site is assumed bound to the graphite (phthalocyanine sits flat on the graphite) through an oxygen atom. If this is the situation, then the oxygen axial linkage to the surface would remain intact through all of the oxidation states. Otherwise, the complex will be essentially completely desorbed after a few voltammetry cycles and possibly even just one cycle in the experiments where the TsPc complex is preadsorbed and not present in the solution. The edge orientation avoids this dilemma. Note further that both Fe(III) and Fe(II) may be six-coordinate but that Fe(I)TsPc is likely only to be four- or five-coordinate [13] depending upon the availability of soft ligands.

Equations (7a) and (7b) reflect an aquo-hydroxy reaction bound to the central iron atom. In the former case, a hydroxyl group balances the positive charge on the cation radical. Equations (7d)–(7f) show formation of anions whose negative charge is balanced by a proton which must presumably sit on a bridging azo nittrogen atom made more basic by the negative charge. The discontinuity between peaks 1 and A in both Fe and CoTsPc across the pH range (Fig. 7) is curious given their similar assignment. The adsorbed species on the electrode in alkaline medium is believed to be essentially non-aggregated while that in acid medium is probably aggregated (see above). Thus if the species are different in the two pH ranges, a discontinuity would certainly be possible; however it is puzzling that it should only occur for one set of peaks.

Similarly if the sulfonic acid residues were all deprotonated in basic medium and all protonated in acid medium, a discontinuity (or sigmoid curve) would be seen. While, as discussed above, we expect the sulfonic acid groups to remain deprotonated until quite low pH, this may not be true for the doubly negatively charged species associated with reduction at peak A. Thus the discontinuity could be a consequence of a rapid changeover from $[Pc(SO_3)]_4^{4-}$ to $Pc(SO_3H)_4$ near pH = 5.

The anomalous high charge of peak 1 for adsorbed Fe-TsPc and Co-TsPc

As indicated earlier concerning Fe-TsPc, the charge under peak 1 in alkaline media is up to ~ 4 times greater than under peaks 2–4, even through all four peaks appear to involve one electron process for Fe-TsPc; Co-TsPc peak 1 also has a anomalous high charge in alkaline media. Any explanation must be compatible with the observation that the Nernst equation indicates a one electron transfer per molecule of the adsorbed complex. There are two limiting explanations:

(i) Peak 1 corresponds to four consecutive one electron transfer reactions of one molecule, all occurring at the same potential; or

(ii) The number of adsorbed molecules which are electrochemically active for the redox process corresponding to peak 1 is four times greater than for the other three peaks at more positive potentials.

There is also a limiting condition that two consecutive one electron transfer

reactions are involved per adsorbed molecule but that twice as many adsorbed molecules are available for the redox process corresponding to peak 1 as for the other three peaks. The possibility that a demetallated species is responsible for peak 1 and is present in higher surface concentration than either Fe- or Co-TsPc seems excluded by the fact that the features of the adsorbed metal free H_2-TsPc are not seen in the voltammograms of the adsorbed Fe and Co complexes. The peaks in the voltammogram for adsorbed H_2-TsPc are not reversible in alkaline or acid media. In the solution phase both an Fe-tetrapyridino-porphyrazine in aqueous solution [59] and Fe-TsPc in organic solvent (acetonitrile) exhibit a ~ 2 electron reduction under a single voltammetry peak. Thus a two electron process is possible at a single potential, but this does not necessarily mean that two consecutive one-electron processes are involved, both occurring at the same potential. Since multiple step one electron transfer processes occurring at the same potential for a given species are very unlikely, possibly (ii) seems more likel. Non-ideal behaviour and deviation from eqn. (2), however, might render the value of $n = 1$ somewhat questionable. Further work is in progress to clarify this situation.

The charge under peaks 2–4 in Figs. 1 and 3, taken with an assumption of 1 electron/molecule, leads to about 1.3×10^{-10} mol/cm^2. If we assume that the observed macroscopic area is the same as the true area, this coverage could be reasonable for a monolayer with the plane of the TsPc ligand perpendicular to the surface. If the process responsible for peak 1 corresponds to one electron per molecule, however, then this would require far more adsorbed TsPc complex than a monolayer. Perhaps the complex is present in stacks on the surface with not all of the molecules active for all of the redox processes.

Oxygen reduction

One of the key questions in the oxygen reduction reaction catalyzed by phthalo-cyanines and other macrocycle complexes is whether the redox potential of the M(III)/M(II) couple is the most important factor in the catalysis. It has been often noted that in the case of Co-complexes in solution phase, there is a qualitative relationship between the oxidation potential of a metal complex and its tendency to undergo a reversible oxygenation reaction. Complexes at which oxidation potentials of the central metal ion are relatively negative such as Mn(II), Fe(II), and Cu(I) tend to the irreversibly oxidized by oxygen. At the other extreme, metals such as Cu(II), Zn(II) or Fe(III) which do not show the metal oxidation voltammetric peaks do not readily react with molecular oxygen in solution phase. Whether the redox potential of the M(III)/M(II) couple governs the interaction between the macrocycle molecule and oxygen, when the former is adsorbed on an electrode surface, is not yet fully understood. Most authors assume that the macrocycles function as redox catalysts; i.e., an obligatory step is the reduction of the metal center (III → II) of the complex prior to the reduction of O_2. Our experiments with Fe- and Co-TsPc also support this mechanism. However, Bettelheim et al. [19] have reported that O_2 reduction catalyzed by Fe(III)-tetra-(o-aminophenyl)porphyrin and Fe(III)-tetra-(N-(2-hy-

droxo-ethyl)pyridyl)porphyrin attached to a glassy carbon electrode starts at potentials somewhat more positive than for the reduction of the two iron centers. Similar results are reported for the adsorbed dicobalt face-to-face porphyrin dimer [18]. These authors claim that the O_2 reduction occurs after the first but prior to the second reduction wave of the metal porphyrin in the absence of O_2. Bettelheim et al. [19] explain this through the formation of an oxygen adduct which has its reduction potential more positive than that of Fe(III)-porphyrin. However, it is unlikely that Fe(III) complexes can form an oxygen adduct. The UV–visible absorption and resonance Raman spectroscopy of Fe(III)TsPc in solution phase [47,49] and electro-reflectance measurements of the adsorbed Fe(III)TsPc at potentials where iron is in the oxidation state (III) [31] did not show evidence of the oxygen adduct formation. On the other hand, the Surface Enhanced Raman Spectroscopy (SERS) study of Fe(III)TsPc adsorbed on silver electrode has shown that an interaction between Fe-TsPc and O_2 exists at potentials where the iron center is in oxidation state (II) and/or (I) [60].

In the case of Co(II)TsPc the oxygen adduct formation has been observed by using UV–visible absorption spectroscopy in solution phase and also when the complex was adsorbed at various electrode surfaces such as Pt, Au and graphite at potentials more positive than those where O_2 reduction takes place [31]. However, it is not known whether the adduct formation also occurs in the O_2 reduction region. The oxidation of Co(II)TsPc by molecular O_2 at such negative potentials is not thermodynamically favorable but a very weak interaction is quite possible. Indeed, the SERS experiments performed a with silver electrode confirmed this possibility [60].

In contrast to the influence, mentioned above, of O_2 on the voltammetric peaks of porphyrin complexes reported by Bettelheim et al. [19], we did not observe any peak potential shift of Fe-, Co- and Cu-TsPc in the presence of O_2 (see Figs. 9 and 10). The only changes in the voltammetric curves induced by O_2 were observed in the case of Co(II)TsPc and these were described above. The anodic irreversible wave observed in the presence of O_2 and H_2O_2 (see Figs. 10–12) was found to correspond to the oxidation of H_2O_2 most probably to the superoxo species, which undergoes further oxidation to O_2 at more positive potentials. In view of the fact that the bare graphite surface does not show any oxidation current for H_2O_2 under the same conditions, Co(II)-TsPc appears to be a catalyst for the H_2O_2 oxidation reaction.

20

REFERENCES

1 A.B.P. Lever, Adv. Inorg. Chem. Radiochem., 7 (1965) 27.
2 K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, New York, 1975.
3 L.J. Boucher in G.A. Melson (Ed.), Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York, 1979.
4 A. Stanieda and G. Biebl, Z. Phys. Chem, 52 (1967) 254.
5 D.W. Clack and N.S. Hush, J. Amer. Chem. Soc., 87 (1965) 4238.
6 D. Lexa, M. Momenteaux and J. Mispelter, Biochim. Biophys. Acta, 338 (1974) 151.
7 L.A. Constant and D.G. Davis, Anal. Chem., 47 (1975), 2253.
8 K.M. Kadish and L.A. Bottomley, J. Amer. Chem. Soc., 99 (1977) 2380.
9 A. Wolberg and J. Manassen, J. Amer. Chem. Soc., 92 (1970) 2982; J. Manassen, J. Catal., 33 (1974) 133.
10 A.B.P. Lever and J.P. Wilshire, Inorg. Chem., 17 (1978) 1145.
11 L.D. Rollmann and R.T. Iwamoto, J. Amer. Chem. Soc., 90 (1968) 1455.
12 d.W. Clack, N.S. Hush and I.S. Woolsey, Inorg. Chim. Acta, 19 (1976) 129.
13 A.B.P. Lever and J.P. Wilshire, Can. J. Chem., 54 (1976) 2514.
14 A.B.P. Lever and P.C. Minor, Proc. IX. Conference on Coordination Chemistry, Bratislava, 1983.
15 A.B.P. Lever and P.C. Minor, Adv. Mol. Relax. Proc., 18 (1980) 115.
16 J. Zagal, R.K. Sen and E. Yeager, J. Electroanal. Chem., 83 (1977) 207.
17 J. Zagal, P. Bindra and E. Yeager, J. Electrochem. Soc., 127 (1980) 1506.
18 J. Collman, P. Denisevich, Y. Konai, M. Marrocco, C. Koval and F.C. Anson, J. Amer. Chem. Soc., 102 (1980) 6027.
19 A. Bettelheim, R.J. Chan and T. Kuwana, J. Electroanal. Chem., 110 (1980) 93.
20 (a) V.R. Shepard and N.R. Armstrong, J. Phys. Chem., 83 (1979) 1268, (b) V.I. Gavrilova, N.V. Butusova, E.A. Luk'yanets, and I.V. Shelepin, Elektrokhimiya, 16 (1980) 1611.
21 J. Zagal, Ph.D. Thesis, Case Western Reserve University, Cleveland, OH, 1978.
22 S. Sarangapani, Ph.D. Thesis, Case Western Reserve University, Cleveland, OH, 1983.
23 H. Jahnke, M. Schonborn and G. Zimmerman, Top. Curr. Chem., 61 (1976) 133.
24 W.R. Harris, G.L. McLendon, A.E. Martell, R.C. Bess and M. Mason, Inorg. Chem., 19 (1980) 21.
25 D.M. Wagnerova, E. Schjwertnerova and J. Veprek-Siska, Collect. Czech. Chem. Commun., 39 (1974) 1980..
26 L.C. Gruen and R.J. Blagrove, Aust. J. Chem., 26 (1973) 319.
27 Simic-Glavaski, S. Zecevic and E. Yeager, J. Electroanal. Chem., 150 (1983) 469.
28 G. McLendon and A.E. Martell, Inorg. Chem., 16 (1977) 1812.
29 D. Vonderschmitt, K. Bernauer and S. Fallab, Helv. Chim. Acta, 48 (1965) 951.
30 T.H. Weber and D.H. Busch, Inorg. Chem., 4 (1965) 469.
31 B.Z. Nikolic, R.R. Adzic and E. Yeager, J. Electroanal. Chem., 103 (1979) 281.
32 F. Cariati, F. Morazzoni and M. Zocchi, J. Chem. Soc. Dalton, (1978) 1018; F. Cariati, F. Morazzoni and C. Buseto, J. Chem. Soc. Dalton, (1976) 496.
33 H. Sigel, P. Waldmeir and B. Prijs, J. Inorg. Nucl. Chem. Lett., 7 (1971) 161.
34 K. Bernauer and S. Fallab, Helv. Chim. Acta, 54 (1961) 1287.
35 R.J. Blagrove and L.C. Gruen, Aust. J. Chem., 25 (1972) 2553.
36 Z.A. Schelly, R.D. Farina and E.M. Eyring, J. Phys. Chem., 74 (1970) 617.
37 E.W. Abel, J.M. Pratt and E. Whelan, J. Chem. Soc. Dalton Trans., (1976) 509.
38 Z.A. Schelly, D.J. Harward, P. Hemmes and E.M. Eyring, J. Phys. Chem., 74 (1970) 3040.
39 R.D. Farina, D.J. Halko and J.H. Swinehart, J. Phys. Chem., 76 (1972) 2343.
40 K. Fenkart and C.H. Brubaker, J. Inorg. Nucl. Chem., 30 (1968) 3245.
41 P.C. Minor, Ph.D. Thesis, York University, Toronto Canada, 1983.
42 A.P. Brown, C. Koval and F.C. Anson, J. Electroanal. Chem., 72 (1976) 379.
43 A.J. Bard and L. Faulkner, Electrochemical Methods, Wiley, New York, 1980, p. 522.
44 B. Simic-Glavaski, S. Zecevic and E. Yeager, 165th National Meeting the Electrochemical Society, Ext. Abstr., 84-1, (1984) 566; in preparation.

45 R.C. Weast (Ed.), Handbook of Chemistry and Physics, 63rd ed., CRC Press, Boca Ratom, FA, 1982–1983.

46 R. Kotz, and e. Yeager, J. Electroanal. Chem., 113 (1980) 113.

47 B. Simic-Glavaski, S. Zecevic and E. Yeager, J. Electroanal. Chem., 150 (1983) 469.

48 B. Simic-Glavaski, S. Zecevic and E. Yeager, J. Amer. Chem. Soc., in press.

49 B. Simic-Glavaski, S. Zecevic and E. Yeager, J. Raman Spectrosc., 14 (1983) 338.

50 R. Adzic, B. Simic-Glavaski and E. Yeager, 165th National Meeting, the electrochemical Society, Ext. Abstr., 84-1 (1984) 597, J. Electrochem. Soc., to be submitted.

51 A. Giraudeau, A. Louati, M. Gross, J.J. Andre, J. Simon, C.H. Su and K.M. Kadish, J. Amer. Chem. Soc., 105 (1983) 2917.

52 P.C. Minor and A.B.P. Lever, in preparation.

53 J.F. Myers, G.W. Rayner-Canham, and A.B.P. Lever, Inorg. Chem., 14 (1975) 461.

54 A.B.P. Lever, S. Licoccia, K. Magnell, P.C. Minor and B.S. Ramaswamhy, CS Symp. Ser., 201 (1982) 237.

55 A.B.P. Lever, W. Liu, M. Melnik and A. Nevin, to be submitted.

56 P. Day, H.A.O. Hill and M.G. Price, J. Chem. Soc., (A) 90 (1968) 670.

57 D.H. Busch, J.H. Weber, D.H. Williams and N.J. Rose, J. Amer. Chem. Soc., 86 (1964) 5161.

58 V.I. Gavrilova, E.A. Luk'yanets, and I.V. Shelepin, Elektrokhim, 17 (1981) 1183; V.I. Gavrilova, L.G. Tomilova, E.V. Chernykh, O.L. Kaliya and I.V. Shelepin, Zh. Obsch. Khim., 50 (1980) 2143.

59 E.B. Yeager et al., in preparation.

60 S. Zecevic, B. Simic-Glavaski and E. Yeager, 164th National Meeting the Electrochemical Society, Ext. Abstr., 83-2, (1983) 769; to be submitted.

END

FILMED

1-86

DTIC